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HOLOGRAPHIC POLYMER DISPERSED LIQUID CRYSTAL (HPDLC) TRANSMISSION GRATINGS FORMED BY VISIBLE LIGHT INITIATED THIOL-ENE PHOTOPOLYMERIZATION (POSTPRINT)

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Holographic polymer dispersed liquid crystal (HPDLC) transmission gratings formed by visible light initiated thiol-ene photopolymerization

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ABSTRACT

We report on the initial development of a visible initiator for thiol-ene photopolymerization using the 647 nm radiation from a Krypton ion laser. The photoinitiator system consists of the dye oxazine 170 perchlorate and the co-initiator benzoyl peroxide. Electron transfer occurs between the singlet excited state of the oxazine dye and benzoyl peroxide with subsequent decomposition of the peroxide yielding benzoyl oxy radicals capable of free radical initiation. We demonstrate that this photoinitiation system enables holographic patterning of HPDLC gratings as initial Bragg transmission gratings with a periodicity less than one micron using 647 nm radiation. These gratings were electrically switchable between a diffractive and transmissive state. Morphology studies using bright field transmission electron microscopy (BFTEM) indicate the phase separation of nearly spherical shaped nematic liquid crystal droplets of several hundred nanometers in diameter. This demonstration suggests that reflection gratings can be written using this photoinitiator system and 647 nm radiation which have switchable notch wavelengths approaching 2 microns.

Key words: photopolymerization, thiol-ene chemistry, transmission grating, HPDLC

1. INTRODUCTION

Holographic polymer-dispersed liquid crystals (HPDLCs) are formed by non-homogeneous spatial illumination of monomer/LC mixtures.¹⁻³ Constructive interference of laser beams on a pre-polymer syrup containing multi-functional monomers, nematic LC, dye and a co-initiator results in the anisotropic distribution of polymer and LC-rich layers leading to a periodic refractive index modulation which can be electrically modulated. The resulting Bragg gratings are electrically switchable and have high potential for devices in a variety of display and communication applications⁴. Crosslinked polymers from multi functional acrylates have been previously employed as hosts for HPDLCs¹⁻³. The use of these multifunctional acrylate monomers as hosts has some disadvantages including very early gelation and subsequent vitrification, low monomer conversion, and post-polymerization reactions⁵. In addition, additives including surfactants and chain extenders are needed to optimize performance³.

Recently, we have demonstrated that most of the drawbacks associated with the use of acrylates as hosts for HPDLCs can be overcome by employing thiol-ene chemistry⁶. Thiol-ene polymers are well known for their role in the preparation of UV curable coatings and adhesives⁷. Thiol-ene polymers are formed by the combination of step growth and free radical reactions between multifunctional aliphatic thiols and vinyl monomers containing 'ene' groups. Free radical producing photoinitiation triggers the

polymerization which is followed by H-atom abstraction and step-chain growth. The thiol-ene reaction is based on a stoichiometric relation between the reacting components; either the thiol or ene must have a functionality >2 for polymer formation and cross-linking. The thiol-ene reaction mechanisms, polymerization kinetics and reactivities of different thiol systems have been reviewed by Jacobine and more recently by Hoyle^{7,8}.

We previously reported on the formation of reflection gratings in thiol-ene polymer/LC composites using a single-beam prism-coupled holographic geometry and 364 nm radiation from an Argon ion laser⁶. Unfortunately, using this chemistry (and thus writing wavelength) limits the upper end of the wavelength of the reflection notch that can be written. Notch wavelengths above 800 nm are difficult to achieve due to the poor overlap of the beams induced by the severe angles needed to red-shift the periodicity. In order to extend the ability of writing notches into the near infra-red and beyond (800-2000+ nm), we developed the visible initiators Rhodamine 6G and Pyromethene 597 which allow for writing to occur using He-Cd (442nm), Argon ion (476, 488, 514 nm) and Verdi (532 nm) laser radiation¹⁰. Reflection notches extending to 1600 nm were written using these visible initiators. Using the further red shifted Krypton ion laser line of 647 nm and this single prism geometry is attractive and should allow one to extend the range of reflection notches to above 2000 nm.

A literature survey reveals no reports of thiol- ene photopolymerization using long wavelength (>600 nm) light sources. In the initial work described here, we demonstrate that the well known laser dye oxazine 170 in combination with a coinitiator, benzoyl peroxide is an efficient initiator for thiol-ene photopolymerization using 647 nm radiation. We demonstrate this capability here in a transmission grating geometry which is easier to initially examine, similar to our approach in previous work on the development of photoinitiators for the He-Cd, Ar+, and Verdi radiation sources⁹. We demonstrate here switchable transmission gratings with weak diffraction efficiency (~10%) of approximately 800 nm period which are fully switchable which were written using the longer wavelength radiation source. The successful demonstration reported here lays the groundwork for future reflection notch fabrication using the same wavelength and photoinitiator using a single prism reflection geometry.

2. EXPERIMENTAL

Oxazine 170 perchlorate (Oxz170), 1-vinyl-2-pyrrolidone, and benzoyl peroxide (BP) were obtained from Aldrich. We employed the commercially available thiol-ene monomer mixture Norland 65, a product of Norland Optical Adhesives Inc. BL037 and E7 from EM industries are eutectic mixtures of cyano substituted biphenyls and terphenyls. Both plain glass and ITO coated glass cells were used as substrates. The pre-polymer syrup containing 5 or 8 micron diameter glass spacers, NOA65 monomer, 0.5% Oxz170, 2.5% benzoyl peroxide and 24% BL037 or 35% E7 was placed between two glass slides and attached to the prism with index matching liquid. The pre-polymer syrup also contained 5% N-vinylpyrrolidinone (NVP) as a reactive diluent to facilitate homogenization. A single-beam prism-coupled holographic geometry was used for writing transmission gratings using the 647 nm line from a Krypton ion laser. Laser writing powers ranged from 100 to 500 mW/cm² with exposure times of 45 seconds. Post-curing was achieved by exposing the grating in white light for an hour. Optical characterization of the transmission gratings was done using a green (532 nm) laser as a probe beam. For electrical switching, a square wave signal at 1 kHz operating from 0 to 200 V RMS was applied and changes in DE were monitored. Samples for microscopy were embedded in flat molds using Epo-fix resin and cured overnight in a 60° C oven. The blocks were trimmed and ultramicrotomed at room temperature using an RMC Ultramicrotome. Sections of 50-60 nm thickness were cut with a 35° Diatome diamond knife, picked up onto 400 mesh grids and vapor stained with RuO₄. The sections were then imaged using bright field transmission electron microscopy (BFTEM) performed on a FEI CM200FEG TEM.

3. RESULTS AND DISCUSSION

Finding suitable dyes for visible laser initiation is indeed challenging since the highly reactive aliphatic thiols react with conventional dyes like xanthene-type systems even in the dark. We demonstrated earlier that the laser dyes Rhodamine 6G (Rh6G) and Pyromethene 597 are chemically reactive when combined with the powerful oxidizing agent BP¹⁰. In the case of Rh6G, the chemical structure is close to that of Oxz170 and spectroscopy studies shown here indicate the photophysics are very similar to that of Rh6G. Addition of BP to Oxz170 leads to the formation of an association complex indicated by the

decrease of the dye absorption as shown in Figure 1. This lowering of the absorption strength is indicative of the formation of a complex possessing a lower molar extinction coefficient as BP does not have absorption beyond 350 nm. The fluorescence is quenched upon addition of BP, shown in Figure 2, indicative of the presence of an excited singlet molecule. Based on these spectroscopic studies, Scheme 1 is postulated as the mechanism enabling reactive free radical generation.

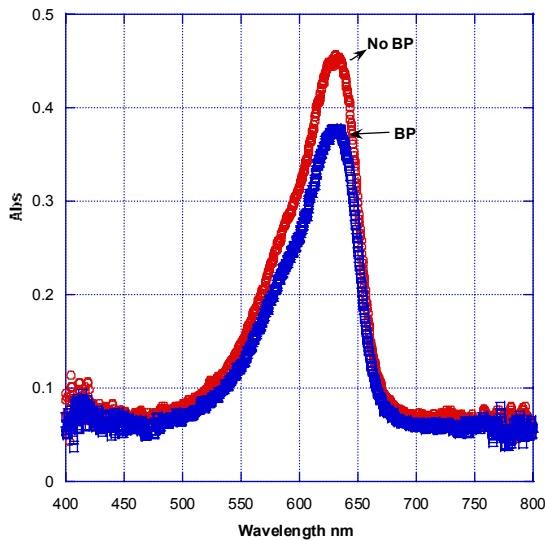


Figure 1. Absorption spectrum of Oxazine 170 perchlorate with and without BP. The spectrum was taken in the NOA65 monomer.

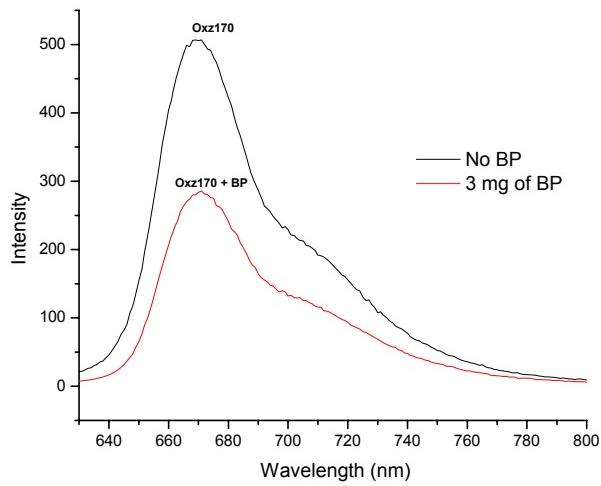
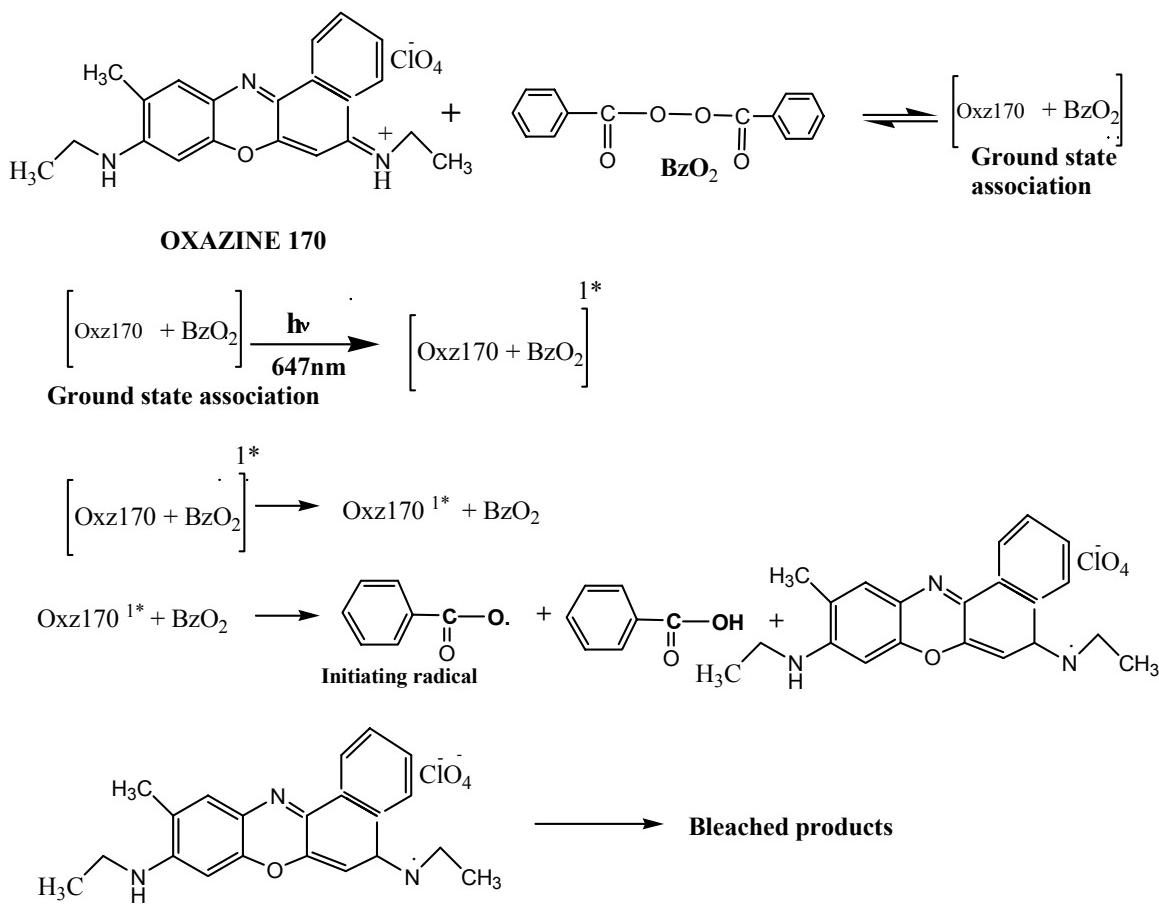


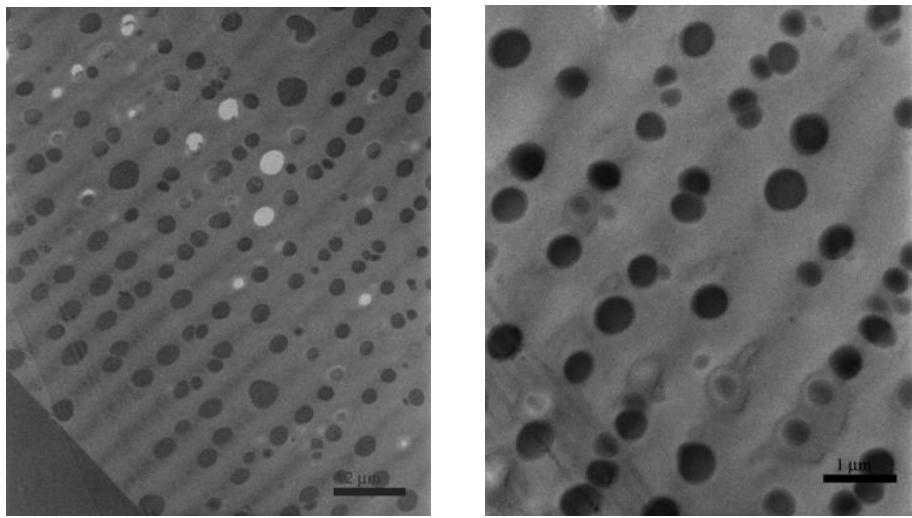
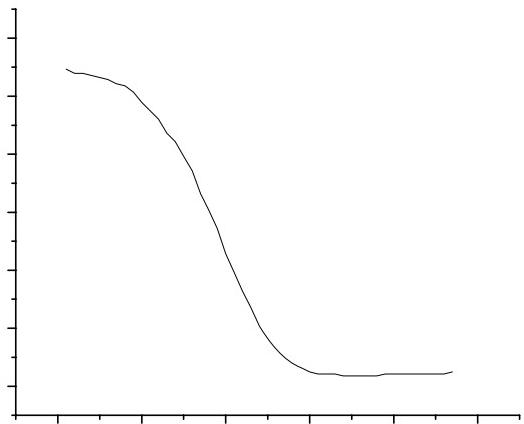
Figure 2. Fluorescence of Oxazine 170 perchlorate with and without benzoyl peroxide. Both samples were added to NOA65.



Scheme 1. Mechanism of free radical formation from the combination of Oxazine 170 perchlorate, benzoyl peroxide, and 647 nm radiation.

Electron transfer occurs from the excited singlet state of Oxz170 to BP, followed by the decomposition of BP giving a benzoyl oxy free radical capable of initiation. (Scheme 1). The benzoyl oxy radical is very efficient for initiation as it can react with the olefinic bond in addition to abstracting a hydrogen atom from the thiol molecule. During the grating formation, efficient bleaching of the Oxz170 is observed.

The combination of Oxz170 and BP proved to be an efficient initiator system as transmission gratings corresponding to the Bragg regime were observed within 10 seconds of the exposure of the pre-polymer syrup containing the LC to 647 nm radiation. Only one diffraction order (at a Bragg angle of 21 degrees) was observed for the grating confirming the Bragg nature of the grating. The grating spacing as measured both optically and morphologically was $\sim 800\text{-}900$ nm. The size of the domains were approximately $\frac{1}{2}$ of the periodicity and as such, the samples exhibited appreciable scatter. This diminished the overall DE and films with only $\sim 10\%$ DE were obtained. Reasonable agreement was seen between the optically calculated spacing and the one derived from TEM micrograph. The grating was electrically switchable with a threshold value for the onset of switching $< 2V/\mu\text{m}$ with complete switching occurring at $9 V/\mu\text{m}$. TEM micrographs shown in Figure 4 clearly show the periodic array of the droplets and the overall nature of the morphology. The LC droplets are dark on a lighter thiol-ene network background. The



4. CONCLUSIONS

We have demonstrated the use of a visible initiator suitable for thiol-ene photopolymerization using the Krypton ion laser line of 647 nm. Bragg transmission gratings were written with the laser dye Oxazine170 perchlorate in combination with benzoyl peroxide. Spectroscopy studies showed ground state association between the dye and the coinitiator benzoyl peroxide. Electron transfer from the excited singlet state of the dye to the coinitiator and subsequent decomposition produced the initiating radical. This radical enabled the holographically patterning of a Bragg transmission grating using thiol-ene monomers mixed with liquid crystals and 647 nm radiation. Electrically switchable Bragg gratings with spacings of ~0.8 micron were fabricated and TEM studies showed the presence of discrete, phase separated, nearly spherical liquid crystal droplets. This successful demonstration of efficient photopolymerization at this wavelength suggests that future reflective HPDLC geometries can be explored.

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REFERENCES

1. (a) Bunning, T. J.; Natarajan, L. V.; Sutherland, R. L.; and Tondiglia, V. P. *Ann. Rev. Mat. Sci.*, **2000**, *30*, 83. (b) Crawford, G. P.; *Opt. Phot. News*, **2003**, p 54.
2. Sutherland, R. L.; Natarajan, L. V.; Tondiglia, V. P.; and Bunning, T. J. *Handbook of Advanced Electronic and Photonic Materials and Devices*, Ed: Nalwa, H. S., Vol. 7, *Liquid Crystals, Displays, and Laser Materials*, Academic Press, San Diego, **2000**, Ch. 2, pp. 68-103.
3. Klosterman, J.; Natarajan, L. V.; Tondiglia, V.P.; Sutherland, R. L., White, T. J.; Guymon, C. A.; Bunning, T. J. *Polymer*, **2004**, *45*, 7213.
4. Sutherland, R. L.; Natarajan, L. V.; Tondiglia, V. P.; Bunning, T. J. *SPIE Proceedings*, **2003**, *5003*, 35.
5. Klosterman, A. M.; Pogue, R. T.; Schmitt, M. G.; Natarajan, L.V.; Tondiglia, V.P.; Tomlin.;D.; Sutherland, R. L.; and Bunning, T.J. *MRS Proc.*, **1999**, *559*, 129.
6. Natarajan, L. V., Shepherd, C. K., Brandelik, D. M., Sutherland, R. L., Chandra, S., Tondiglia, V. P.; Tomlin, D.; and Bunning, T. J. *Chem. Mater.* **2003**, *15*, 2477.
7. Jacobine, A. F. In *Radiation curing in polymer science and technology III*; Fouassier, J. D., Rabek, J. F., Eds., Elsevier Applied Science; London, **1993**, Chapter 7, p219.
8. Hoyle, C. E.; Lee, T. Y.; Roper. T. J. *Polym. Sci., Part A Polym. Chem.*, **2004**, *42*, 5301.
9. Natarajan, L. V., Tondiglia,V. P., Sutherland, R. L., Tomlin.D., and Bunning, T. J., *MRS Proc.*, **2003**, *776*, 225-30.
10. Natarajan, L.V., Brown, D.P., Wofford, J.M., Tondiglia, V.P., Sutherland, R.L., Lloyd, P.F., Bunning, T.J. *Polymer*, **2006**, *47*, 4411.